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B1E
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(71) Applicants
The British Petroleum
Company Limited,
Britannic House, Moor
Lane, London EC2Y 9BU
(72) Inventors
William John Ball,
Leonard Cotton,
David Gordon Stewart
(74) Agent
J. Harry,
BP International Limited,
Patents and Licensing
Division, Chertsey Road,
Sunbury-On-Thames,
Middlesex TW16 7LN

(54) Production of alcohols from
synthesis gas

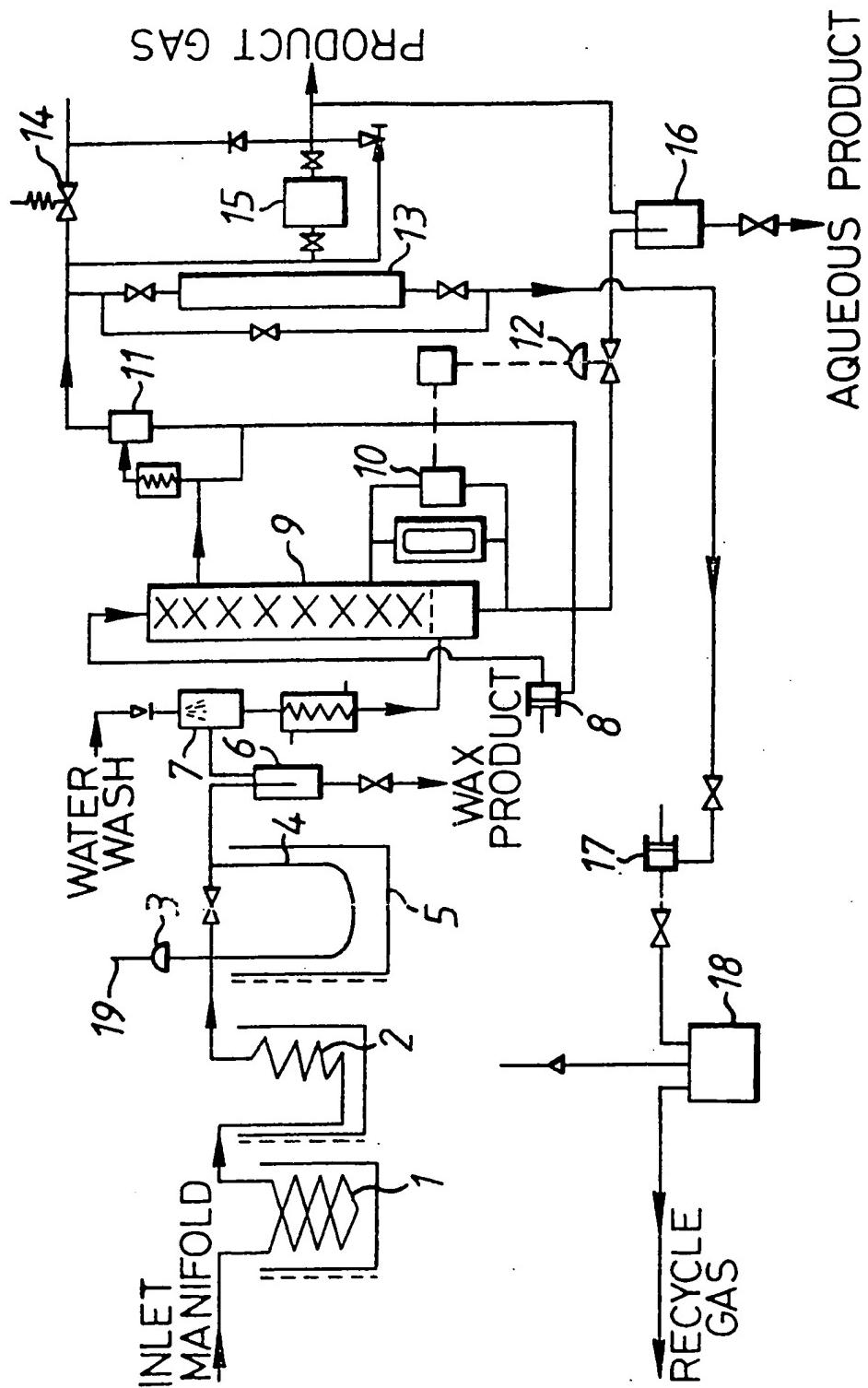
(57) A mixture of alcohols principally comprising methanol and ethanol is produced by reacting carbon monoxide with hydrogen in the presence as catalyst of a supported mixture of a rhodium component and a rhenium component, optionally also containing one or more of the metals

iron, manganese, molybdenum, tungsten, ruthenium, chromium, zirconium, uranium and thorium. Support materials include silica, alumina, silica/alumina, magnesia, thoria, titania, chromia, zirconia and active carbon. Typically the reaction conditions are a temperature in the range from 150 to 450°C, a pressure in the range from 1 to 700 bars and a gas hourly space velocity greater than 10³ vol/vol/hour.

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SPECIFICATION

Process for the production of alcohols by the catalytic conversion of synthesis gas

The present invention relates generally to a process for the production of oxygenated hydrocarbons and in particular to a process for the production of a mixture of alcohols principally comprising methanol and ethanol by contacting a mixture of carbon monoxide and hydrogen, hereinafter to be referred to as synthesis gas, with a catalyst comprising a supported mixture of a rhodium component and a rhenium component.

Methanol and ethanol are valuable industrial products. On a commercial scale methanol is generally manufactured from synthesis gas and ethanol is produced either by fermentation of natural products, e.g. molasses, or by hydration of ethylene in the presence of an acid catalyst. The dwindling reserves of crude oil from which some of the above feedstocks are derived and the associated need to utilise fully the remaining natural resources such as coal and the vast amounts of gases, e.g. methane potentially available from the exploitation of North Sea oilfields, has stimulated research into the utilisation of synthesis gas which can readily be obtained not only from crude oil but also from both coal and methane gas. Much of the early work on synthesis gas conversion involved the use as catalysts of the iron group metals, ruthenium and various metal oxide systems. One general disadvantage of such systems is that catalysts which possess acceptable activity generally tend to be unselective i.e. they produce a wide spectrum of products including both hydrocarbons and oxygenated hydrocarbons having a broad distribution of carbon members. This not only complicates the recovery of the desired products but also results in wastage of reactants to undesirable products. On the other hand those catalysts having acceptable selectivity generally have a low activity thereby necessitating recycle of large quantities of uncharged reactants.

In US Patent No: 4246186 (Union Carbide Corp) there is disclosed a process which, it is claimed, overcomes the aforesaid disadvantages of the prior art processes. The process for selectivity producing C₂ — oxygenated hydrocarbons involves continuously contacting synthesis gas with a heterogeneous catalyst essentially comprising rhodium metal under reaction conditions correlated so as to favour the formation of a substantial proportion of acetic acid, ethanol and/or acetaldehyde. Subsequent patent applications describe the production of ethanol by contacting synthesis gas with a rhodium/iron catalyst (US Serial No: 541,660 published as a priority document for Netherlands Application No: 7500918), a rhodium/manganese catalyst (DT 4096164), a rhodium/ruthenium catalyst (USP 4101450) and a rhodium/uranium/thorium catalyst (USP 4162262). Furthermore European patent publication No. 0010295 (application No. 79104009.0) (Hoechst) describes the production of ethanol by reacting synthesis gas with a supported mixture of rhodium and one or more of the elements zirconium, hafnium, lanthanum, platinum, chromium and mercury.

We have now found that synthesis gas can be converted to a mixture of alcohols principally comprising methanol and ethanol by contact with a supported mixture of a rhodium component and a rhenium component as catalyst.

Accordingly, the present invention provides a process for the production of a mixture of alcohols principally comprising methanol and ethanol which process comprises contacting synthesis gas with a catalyst comprising a supported mixture of a rhodium component and a rhenium component under reaction conditions which favor the formation of alcohols.

Mixtures of the gases hydrogen and carbon monoxide are abundantly available in the form of synthesis gas. Methods for preparing synthesis gas are well-known in the art and usually involve the partial oxidation of a carbonaceous substance, e.g. coal. Alternatively synthesis gas may be prepared, for example, by the catalytic steam reforming of methane. Although it is preferred to use substantially pure synthesis gas the presence of such impurities as carbon dioxide and nitrogen can be tolerated. On the other hand impurities which have a deleterious effect on the reaction should be avoided. The ratio of hydrogen to carbon monoxide in the synthesis gas may vary widely. Normally the molar ratio of hydrogen to carbon monoxide may be in the range from 20:1 to 1:20, preferably from 5:1 to 1:5 and even more preferably from 1:1 to 2:1. Increasing the molar ratio of hydrogen to carbon monoxide beyond 2:1 generally tends to increase the total rate of reaction but only at the expense of an increase in selectivity to methane. Increasing the molar ratio of hydrogen to carbon monoxide also favours the formation of more highly reduced oxygenated products. Thus as the ratio increases so the formation of ethanol, rather than acetaldehyde or acetic acid, is favoured. Methods for adjusting the molar ratio by the so-called 'shift reaction' are well-known to those versed in the art.

The catalyst comprises a supported mixture of a rhodium component and a rhenium component. A wide variety of support materials may be employed. Suitable support materials include silica, alumina, silica/alumina, magnesia, thoria, titania, chromia, zirconia and active carbon of which silica is preferred. Molecular sieves and crystalline zeolites may also be employed. Suitably the support has a relatively high surface area. The support may have a surface area up to 350 square metres per gram (BET low temperature nitrogen adsorption isotherm method), preferably in the range 1 to 300 square metres per gram. Whilst the actual form of the rhodium and rhenium components under the reaction conditions is not known with any degree of certainty it is probable that they are in the oxide form and possibly in the metallic form under the reducing conditions prevailing. Thus the rhodium and rhenium components may

- be added in the form of the metals themselves or in the form of metal compounds and may be added concurrently or sequentially. The rhodium and rhenium components may be deposited on the support by any of the techniques commonly used for catalyst preparation. Although it is possible to add particles of the metals to the support it is preferred to use the techniques of impregnation from an organic or 5 inorganic solution, precipitation, coprecipitation or cation exchange. Conveniently the catalyst may be prepared by impregnating the support with a solution of an inorganic or organic rhodium and rhenium compound. Suitable compounds are the salts of the metals e.g. the halides, particularly the chlorides and nitrates. Following impregnation the catalyst is preferably dried and calcined. The amount of each of 10 the rhodium component and the rhenium component on the support may suitably be in the range of from 0.01 to 25 weight percent, preferably from 0.1 to 10 weight percent, of the metal based on the combined weight of the metals and the support. Additional metal components may also be incorporated 15 in the catalyst. Suitable metals include iron, manganese, molybdenum, tungsten, ruthenium, chromium, zirconium, uranium and thorium, suitably in an amount in the range from 0.1 to 10 weight percent based on the combined weight of the metals and the support.
- 15 The support may also be activated by the addition of a suitable metal or non-metal component prior to incorporation of the rhodium and rhenium components. Whilst a wide variety of such metals and non-metals may be added, the alkali metals, thorium, manganese, rhodium, iron, chromium, molybdenum, zirconium, boron and phosphorus are specific examples of such materials. Any of the known techniques for catalyst preparation hereinafter referred to may be used for addition of the 20 activating material. In the case of a metal activator the support is preferably impregnated with a solution of a compound of the metal, suitably the nitrate or chloride, and is thereafter dried, suitably by evaporation, and calcined. The activated support is then in a suitable condition for addition of the rhodium and rhenium components and optionally other metal components. The amount of activator added may suitably be in the range 0.01 to 50 weight percent, preferably from 1 to 25 weight percent 25 of the activator element, based on the combined weight of the activator element and the support.
- With regard to the reaction conditions the temperature may suitably be in the range from 150 to 450°C, preferably from 200 to 400°C and even more preferably from 200 to 300°C. The use of higher temperatures within the aforesaid range tends to increase the co-production of methane. Because of the highly exothermic nature of the reaction the temperature requires careful control in order to prevent a 30 runaway methantation, in which methane formation increases with increasing temperature and the resulting exotherm increases the temperature still further. In fixed bed operations, temperature control may be achieved by mixing the catalyst with an inert diluent, thereby ensuring that the exothermic heat is more evenly distributed. In this way the catalyst may be protected and its useful life prolonged. Reaction pressure is suitably in the range from 1 to 700 bars, preferably from 20 to 300 bars.
- 35 An important reaction parameter is the conversion. A low conversion, preferably less than 20% of the carbon monoxide, favours the formation of alcohols such as methanol and ethanol. A low conversion may suitably be achieved in a continuous process by employing a high space velocity. Suitably the gas hourly space velocity (volume of synthesis gas, at STP per volume of catalyst per hour) is greater than 10³ vol/vol/hour, preferably in the range from 10⁴ to 10⁶ vol/vol/hour. Excessively high space velocities 40 result in an uneconomically low conversion while excessively low space velocities result in a loss of selectivity to desirable products.

Although the reaction may be carried out batchwise it is preferably carried out in a continuous manner.

The catalyst may be employed in the form of a fixed or a fluidised bed. The desired product may be recovered from the effluent from the reaction by various means, such as scrubbing and/or distillation. 45 The residual gas which consists mainly of unreacted synthesis gas may be mixed with fresh carbon monoxide and hydrogen to give the required feed ratio and this composite gas then recycled to the reaction. Besides methanol and ethanol there may also be produced small amounts of higher alcohols, i.e. C₃ and C₄ — alcohols. The individual alcohols may be recovered from the product mixture by 50 distillative methods well-known in the art.

The process of the invention will now be illustrated by the following Example and by reference to the accompanying Figure which is a simplified flow diagram of the apparatus employed.

With reference to the Figure, 1 is a preheater (150°C), 2 is a preheater (200°C), 3 is a bursting disc, 4 is a reactor, 5 is a salt pot, 6 is a knock-out pot, 7 is a water quench, 8 is a water recycle pump, 9 55 is a water wash tower, 10 is a DP level controller, 11 is a knock-out pot, 12 is a Foxboro valve, 13 is a molecular sieve drier, 14 is a Gyp relief valve, 15 is a back pressure regulator, 16 is an aqueous product receiver, 17 is a gas recycle pump, 18 is a ballast vessel and 19 is a vent.

Also in the Example the terms CO conversion and selectivity will be used. For the avoidance of doubt these are defined as follows:

$$60 \text{ CO Conversion} = \frac{\text{Moles of carbon monoxide consumed}}{\text{Moles of carbon monoxide fed}} \times 100 \quad 60$$

$$\text{Selectivity} = \frac{\text{Moles of carbon monoxide converted to particular product}}{\text{Moles of carbon monoxide consumed.}} \times 100$$

Catalyst Preparation

Rhenium/molybdenum/rhodium/silica.

Ammonium perrhenate (0.72 g), ammonium heptamolybdate tetrahydrate (0.42 g) and rhodium

- 5 trichloride trihydrate (0.65 g) were dissolved in deionised water (20 ml) and added to Davison silica, grade 59 (10 g, 8—16 mesh granules). The mixture was evaporated to dryness on a steam-bath and dried at 120°C for 16 hours. The catalyst was then heated at 450°C in hydrogen for 2 hours at atmospheric pressure and then for 6 hours under a pressure of 4 bars. 5

EXAMPLE

- 10 With reference to the accompanying Figure a mixture of carbon monoxide and hydrogen in a 10 molar ratio of 1:2 was passed via the inlet manifold through the two preheater coils (1) and (2) maintained at 150°C and 200°C respectively in silicone oil baths. The heated gases were then fed via a heat-traced line to the copper-lined reactor (4) containing a fixed bed of the rhenium/molybdenum/rhodium catalyst, prepared in the manner described above, in the form of 8 to 16 mesh (BSS) granules. The reactor was maintained at the desired reaction temperature by immersion in a molten salt bath (5). The product gases were passed via a heat-traced line through a knock-out pot for 15 wax products (6) to a small quench vessel (7) into the top of which water was sprayed. The gases were then passed through a water cooler to the bottom of the water wash tower (9) which was packed with 3/8 inch Raschig rings. In the tower (9) the product gases were washed counter-current with water. 15
- 20 The resulting liquid product was fed into the receiver (16) and any dissolved gases were recombined with the product gas stream from the back pressure regulator (15). The separated gas stream from the top of the water wash tower (9) was passed through a water cooler to the knock-out pot (11) and then to the inlet side of the dome-loaded back pressure regulator (15). Recycle gas was recovered from the inlet side of the back pressure regulator (15), passed through a molecular sieve drier (13) and compressed up to 6.7 bars in the gas ballast vessel (18) using the gas recycle pump (17). The recycle 20 gas was fed back to the inlet manifold. Provision was made to feed spot samples of the inlet gases and the total gas stream to a gas chromatographic analytical unit. 25
- 25 The product gas stream leaving the back pressure regulator (15) was measured and samples were withdrawn and analysed by gas chromatography. The liquid product was also sampled and analysed by 30 gas chromatography.
- When the reactor had reached equilibrium a balanced run was carried out over a one hour period 30 at a temperature of 260°C. A further run was carried out at 277°C. The results obtained are given in the following Table.

TABLE

Reaction parameters:
 GHSV = 47000
 $H_2:CO$ molar ratio = 2:1
 Pressure = 50 bar
 Recycle gas. ratio = 18:1

Reaction Temperature °C	CO Conversion %	SELECTIVITY %						
		Carbon Dioxide	Methane	Ethane	Propane	Methanol	Ethanol	n-Propanol
260	24	12	19	4	3	49	10	4
277	34	13	25	5	3	44	8	2

CLAIMS

1. A process for the production of a mixture of alcohols principally comprising methanol and ethanol which process comprises contacting synthesis gas with a catalyst comprising a supported mixture of a rhodium component and a rhenium component under reaction conditions which favour the formation of alcohols. 5
2. A process according to claim 1 wherein the molar ratio of hydrogen to carbon monoxide is in the range from 1:1 to 2:1. 5
3. A process according to either claim 1 or claim 2 wherein the support is silica.
4. A process according to any one of the preceding claims wherein the support has a surface area 10 in the range 1 to 300 square metres per gram.
5. A process according to any one of the preceding claims wherein the amount of each of the rhodium component and the rhenium component on the support is in the range from 0.1 to 10 weight percent of each metal based on the combined weight of the metals and the support. 10
6. A process according to any one of the preceding claims wherein the catalyst also contains one 15 or more additional metal components selected from iron, manganese, molybdenum, tungsten, ruthenium, chromium, zirconium, uranium and thorium in an amount in the range from 0.1 to 10 weight percent based on the combined weight of the metals and the support. 15
7. A process according to any one of the preceding claims wherein the support is activated by the addition of either an alkali metal, thorium, manganese, rhodium, iron, chromium, molybdenum, 20 zirconium, boron or phosphorus prior to addition of the rhodium and rhenium components. 20
8. A process according to claim 7 wherein the amount of activator added is in the range from 1 to 25 weight percent based on the combined weight of the activator element and the support. 25
9. A process according to any one of the preceding claims wherein the reaction conditions which result in the formation of alcohols are a temperature in the range 150 to 450°C, a pressure in the range 25 1 to 700 bars and a gas hourly space velocity greater than 10^3 vol/vol/hour.
10. A process according to claim 9 wherein the reaction conditions are a temperature in the range 200 to 400°C, a pressure in the range from 20 to 300 bars and a gas hourly space velocity in the range from 10^4 to 10^6 vol/vol/hour. 25

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